P-V-T relations of aqueous sodium hydroxide and its causticity at high temperatures and high pressures

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P-V-T RELATIONS OF AQUEOUS SODIUM HYDROXIDE AND ITS CAUSTICITY AT HIGH TEMPERATURES AND HIGH PRESSURES

By Ryo Kiyama and Shigeto Kitahara*

Introduction

The vapor pressure of aqueous solution of sodium hydroxide has already been studied[1] in the wide range of concentration at temperatures up to 350°C but at higher temperatures than this the *P–V–T* relations of this aqueous solution have never been reported. In the present investigation, the *P–V–T* relations of aqueous solution of sodium hydroxide were measured in the range of temperature from 200°C to 500°C. Besides the *P–V–T* measurements, the authors investigated the corrosion of copper and silver in aqueous solution of sodium hydroxide at high temperatures and high pressures.

Part I *P-V-T* relations of aqueous solution of sodium hydroxide at high temperatures and high pressures

Experimentals

Samples The aqueous solution used in the present investigation is prepared from the upper transparent part of an aqueous saturated solution of sodium hydroxide which is left as it is for several days in order to eliminate the carbonate. The content of the carbonate in the aqueous solution thus prepared and used as the sample is less than 0.5 per cent. The aqueous solution prepared from metallic sodium is also used as the sample but there is no change in the results due to the different preparation methods of the aqueous solution.

Apparatus The apparatus used is the same as in the investigation of the *P–V–T* relations of steam[2] except in the case of the inner surface of the autoclave and the cover coated with silver plate of 0.5 mm thickness in order to avoid corrosion. Any change on the silver plate could not be found after experiment. The pressure gauges used are 100, 300, 500 and 1000 kg/cm² in maximum scale and their maximum errors are ±0.3, ±0.8, ±1.5 and ±3.0 kg/cm² respectively.

Procedures Measurements are made by the method of constant volume. A given quantity of concentrated aqueous solution of sodium hydroxide, the concentration of which has been determined beforehand, is put into the autoclave and the air in the autoclave is exhausted with a vacuum pump, while the autoclave is cooled in ice water. Then a necessary quantity of water is introduced into the autoclave through a valve so that the concentration of the aqueous solution becomes the value required before the experiment. The methods of the measurement of pressure

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1) *Int. Crit. Tables*, 3, p. 370

2) R. Kiyama, H. Kinoshita and S. Kitahara, *This Journal*, 25, 21 (1955)

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and temperature are all the same as in the previous experiment on steam[2]. After each measurement, the aqueous solution is taken out of the autoclave and it is assured that there is no change of the quantity of the solution. The measurements are made in the following conditions; packing ratio: 1/5, 1/3 and 1/2 ml/ml, the concentration of sodium hydroxide: 5, 15, 25, 35 and 45%, temperature: at every interval of 20° from 200°C to 500°C.

Results and Considerations

The results of the measurements are given in Table 1. Fig. 1 to Fig. 3 show the *P-T* relations at each concentration, packing ratio being 1/5, 1/3 and 1/2 ml/ml respectively. As it is shown in Table 1 and Fig. 4, the change of the equilibrium pressure by the packing ratio is rather

Table 1 Vapor pressure of aqueous sodium hydroxide in atmosphere at each condition

Temp. °C \ Conc. % \ Pack. ratio	5			15			25			35			45		
	1/5	1/3	1/2	1/5	1/3	1/2	1/5	1/3	1/2	1/5	1/3	1/2	1/5	1/3	1/2
200	—	—	14.5	—	—	13.1	—	—	11.1	—	—	9.2	—	—	5.8
220	—	—	22.3	—	—	19.4	—	—	17.4	—	—	14.5	—	—	9.2
240	—	—	31.9	—	—	28.6	—	—	25.2	—	—	20.0	—	—	14.5
260	—	—	44.5	—	—	39.7	—	—	35.3	—	—	30.0	—	—	21.3
280	—	—	61.0	—	—	54.7	—	—	48.4	—	—	41.6	—	—	30.5
300	80.3	80.3	81.3	72.6	72.6	73.6	61.0	62.9	63.9	51.3	53.2	55.2	38.7	41.6	41.6
320	107	107	108	94.9	94.9	97.8	81.3	84.2	86.1	66.8	69.7	71.6	51.3	53.2	54.2
340	139	139	141	124	126	128	107	109	111	87.1	91.0	92.9	67.7	69.4	71.6
360	175	176	179	157	160	156	136	140	145	111	116	121	85.2	89.1	93.9
380	213	218	226	192	199	208	164	174	182	136	145	153	105	112	119
400	251	270	284	225	246	259	193	215	229	163	181	191	128	139	146
420	284	323	358	257	293	321	224	257	279	190	218	232	152	168	181
440	313	379	449	288	345	397	254	302	339	218	258	281	176	199	218
460	349	436	542	320	396	474	284	349	406	246	299	335	201	234	260
480	380	494	639	351	449	558	314	400	474	274	344	394	229	271	305
500	411	554	738	382	502	645	344	450	556	303	390	463	258	311	354

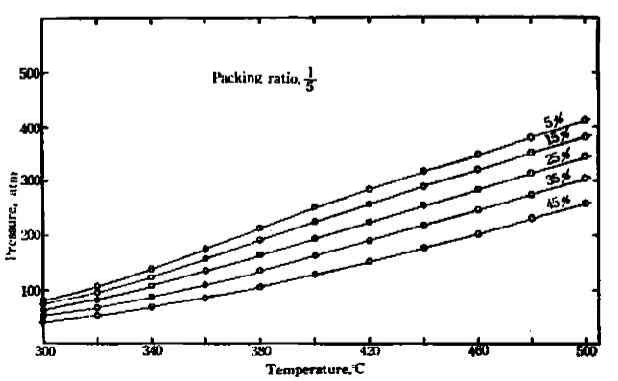

Fig. 1 Pressure-temperature curves at 1/5 packing ratio

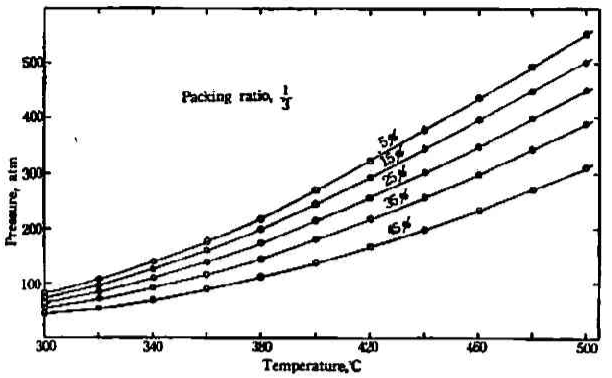

Fig. 2 Pressure-temperature curves at 1/3 packing ratio

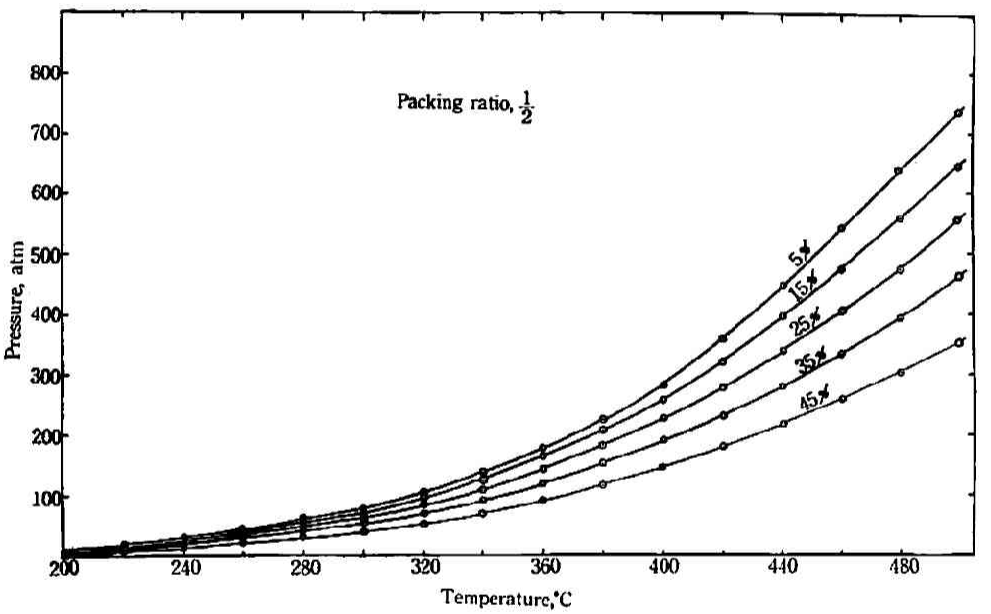

Fig. 3 Pressure-temperature curves at 1/2 packing ratio

small at low temperatures but this change of the equilibrium pressure becomes very large at every concentration at high temperatures. The effect of the packing ratio on the equilibrium pressure obviously results in the vaporization of water and the consequent increase of the concentration of sodium hydroxide in liquid aqueous solution. The comparison of the results of the present investigation with the already published data at 200°C is given in Fig. 5, where the packing ratio of the present data is 1/2 ml/ml. The lower values of the present data are clearly due to the reason above mentioned, that is, the vaporization of the water. However, the authors consider that the data of the present investigation, *P-T*-total volume-initial concentration relations, is very useful especially for practical purposes, although the *P-T*-concentration relations could not be derived because the data of other properties, especially the data of the density of aqueous solution of sodium hydroxide at high temperatures is not available at present.

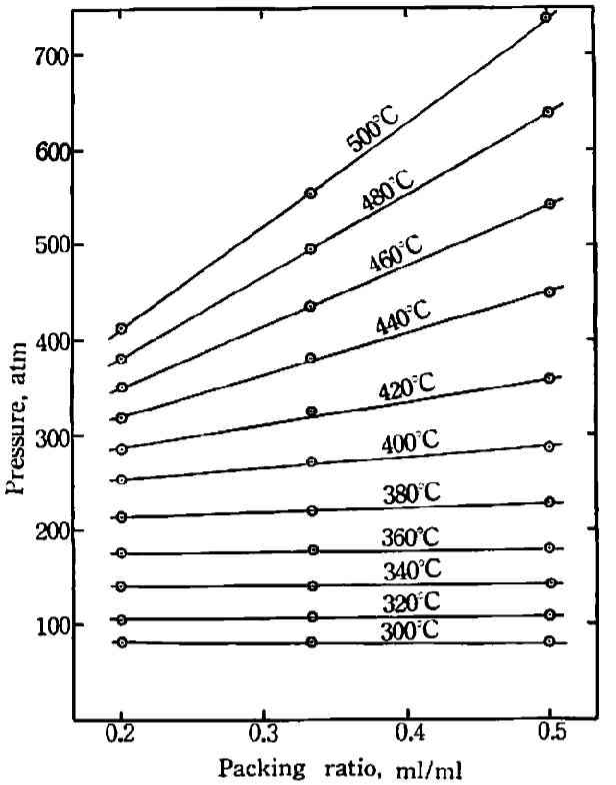

Fig. 4 Relations between packing ratio and equilibrium pressure, at 5% initial NaOH concentration

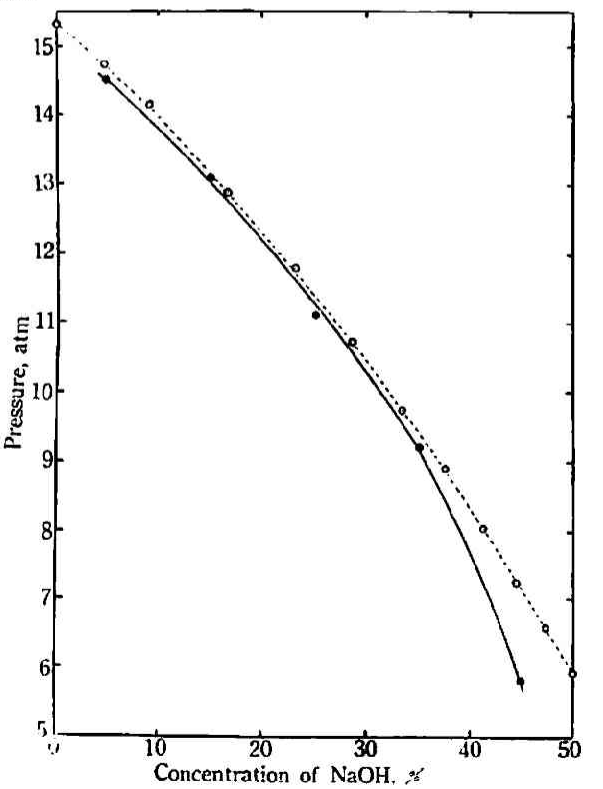

Fig. 5 Comparison of the equilibrium pressure of aqueous sodium hydroxide solution of the present investigation with the published data[1] at 200°C

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Part II Corrosion test of copper and silver in aqueous solution of sodium hydroxide at high temperatures and high pressures

Experimentals

Samples Copper pieces purchased are polished by electrolysis according to an ordinary method, their thickness being 0.6 mm. Silver pieces purchased are also polished mechanically with red ochre. their thickness being 0.5 mm.

Procedures The test is conducted according to Perry's *Chem. Eng. Handbook*[3]. After the polished test piece is washed carefully in water and then in alcohol, the piece is dried at 80°C in an air bath and then cooled in a desiccator. After it gets cool, the piece is weighed. The procedure of the load of aqueous sodium hydroxide solution in the autoclave is the same as in the previous Part I. After the system is kept at constant temperature during definite hours, it is cooled and washed carefully in water, 1 *N* aqueous acetic acid solution, water and finally in alcohol and dried and weighed. Thus, the loss in the weight of the test piece due to the corrosion in the aqueous sodium hydroxide solution at high temperatures and high pressures is obtained. The piece must be washed in 1 *N* aqueous acetic acid solution because very thin covering

Table 2. Corrosion of copper piece in aqueous solution of sodium hydroxide

Conc. of solu. %	Temperature °C	Pressure atm	Loss in weight of test piece 10^{-3} g
5	200	15	0.3
〃	300	81	0.5
〃	350	155	0.7
〃	400	284	2.1
〃	450	489	2.6
〃	500	738	3.4
10	200	14	0.3
〃	300	77	0.8
〃	350	149	1.8
〃	400	271	2.6
〃	450	463	4.0
〃	500	685	5.9
15	200	13	0.4
〃	300	74	0.8
〃	350	145	1.7
〃	400	259	2.7
〃	450	435	4.1
〃	500	645	5.9

Weight of test piece: 0.84~0.85 g, Area of test piece: 0.59 inch^2,
Time of reaction: 48 h, Packing ratio of solution: 1/2

3) J. H. Perry, *Chemical Engineers' Handbook*, p. 1458 (1950)

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Table 3. Corrosion of copper piece in aqueous solution of sodium hydroxide

Temp. °C	Conc. of solu. %	Time of reaction hour	Loss in weight of test piece 10^{-3}g
350	5	6	0.3
〃	〃	12	0.4
〃	〃	48	0.7
〃	15	6	0.8
〃	〃	12	1.1
〃	〃	48	1.7
400	5	12	1.1
〃	〃	48	2.1
〃	10	12	1.9
〃	〃	48	2.6
〃	15	12	1.9
〃	〃	48	2.7

Weight of test piece: 0.84~0.85g, Area of test piece: 0.59 inch^2,
Packing ratio of solution: 1/2

on copper surface is found. Of course, it is checked that there is no change in the weight of copper piece after it is kept in 1 *N* acetic acid solution for several hours.

Results

The results are given in Tables 2 and 3 when the copper piece is used. As it is shown in Table 2, the effect of the concentration of sodium hydroxide is large in 10% solution than in 5% solution, but no significant difference can be found between in 10% solution and in 15% solution. As it is expected, the degree of the corrosion is rapidly increased with increased temperature and corrosion is rapid in the earlier time of the reaction.

The loss in weight of silver pieces can not be found at 350°, 450° and 500°C and there is no trace of silver in the liquid solution when it is checked according to the potassium chromate method.

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